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⑭プラズマＣＶＤ処理装置

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１．発明の名称

プラズマＣＶＤ処理装置

２．特許請求の範囲

（１）気密容器と、該気密容器内を所望の雰囲気にする手段と、該気密容器内に配設された被処理材料と、該被処理材料を陰極に気密容器を陽極にして高電圧を印加し直流プラズマを発生させる直流高圧電源と、前記被処理材料の表面に生成すべき膜の成分を有するガスを前記気密容器内に導入する手段とを備えた装置において、前記気密容器と被処理材料との間に熱電子陰極を設け、該熱電子陰極に気密容器と被処理材料との中間の電圧を印加する直流電源を具備することを特徴とするプラズマＣＶＤ装置。

（２）前記気密容器の内面に沿ってガス噴射ノズルを形成し、該ノズルと被処理材料との間に前記熱電子陰極を設け、該ノズルに向けて熱電子放電を行なう特許請求の範囲第１項記載のプラズマＣＶＤ処理装置。

（３）前記ノズルは環状であり、所望ガスと被膜成分とを含む混合ガスを噴射する特許請求の範囲第２項記載のプラズマＣＶＤ処理装置。

（４）前記熱電子陰極は複数個配置されている特許請求の範囲第１項乃至は第３項の何れかに記載のプラズマＣＶＤ処理装置。

３．発明の詳細な説明

本発明は直流グロー放電により金属のハロゲン化物や弗化物をイオン化し、被処理材料表面に金属若しくは金属窒化物、炭化物等の被膜を生成するプラズマＣＶＤ処理装置に関する。

近時、真空蒸着に比し、形成された膜の性質が非常に良いことからプラズマ中のイオンの照射を利用して金属化合物等の成膜を行なう、所謂プラズマＣＶＤ処理装置（プラズマ中化学気相成長装置）が注目され、既に実用化の段階に入ろうとしている。

直流グロー放電を利用するプラズマＣＶＤ装置においてはグロー放電のイオンの持つ運動エネルギーによって被処理材料を加熱し、導入ガスであ

る窒素ガス、水素ガス及び金属ハロゲン化合物若しくは非化物のガスをイオン化させることによって被処理材料表面に所望化合物の薄膜を生成するようしているが、金属分子のイオン化を高めるために平均電子温度をできるだけ高めることが必要である。この平均電子温度Teは

Te＝q／k 0.3√Mm／Me λe E／P

で現わされる。ここで、qは電子の電荷、kはボルツマン定数、Mm，Meは夫々の気体分子及び電子の質量、λeは0℃，1Torrにおける電子の自由行程、Eは電界強度、Pは圧力である。

上式より、平均電子温度TeはE／Pのパラメータに支配されているが、Eを大きくするには限界があり、従来よりTeを大きくするために圧力Pを小さくすることが実行されている。

しかし、この様にしても直流グロー放電によるイオン化率は低く、高々数%に過ぎないので薄膜の付着レートは非常に低い。プラズマCVDの場合、導入ガス量はイオン化率若しくはプラズマ電力に依存しているため、付着レートを増大しようとしてガス圧を高め、過剰ガスを導入すると未反応物が析出し、被膜としては形成困難になる。従って、ガス圧を低くすることは重要な要件であるが、ガス圧が低いと負グロー幅が広くなり、被処理材料コーナー部の付きまわりが悪くなると言う不具合が生ずる。

本発明は上記従来の欠点を解消し、プラズマCVD処理の被膜付着の迅速化を図り、短時間で均一にして充分な厚さの被膜層を形成し得るプラズマCVD処理装置を提供することを目的とするものである。

本発明の構成上の特徴は気密容器と、該気密容器内を所望の雰囲気にする手段と、該気密容器内に配設された被処理材料と、該被処理材料を陰極に気密容器を陽極にして高電圧を印加し直流プラズマを発生させる直流高圧電源と、前記被処理材料の表面に生成すべき膜の成分を有するガスを前記気密容器内に導入する手段とを備えた装置において、前記気密容器と被処理材料との間に熱電子陰極を設け、該熱電子陰極に気密容器と被処理材料との中間の電圧を印加する直流電源を具備したプラズマCVD装置に存する。

以下図面に基づき本発明を詳説する。

第1図は本発明の一実施例の構成略図、第2図は第1図のA－A断面図であり、1は気密容器を示している。該気密容器は排気管2を介して真空ポンプ3に接続しており、内部が高真空に排気可能である。前記気密容器は第2図から解るように筒状をなしており、その中心部に電気導電性の被処理材料ホルダー4が設置されている。このホルダーには多数の被処理材料5が積載されている。前記ホルダー4は電気絶縁物を介して気密容器1に取付けられており、直流高圧電源6の負端子に接続されている。該高圧電源の正端子は気密容器1に接続され、アースされている。前記気密容器の内面に接して環状のガスノズル7が同電位で設けられ、容器外のガス導入源8より導入されたプラズマCVDに必要なガスが多数の微細穴より容器の中心に向けて噴射される。前記ガス導入源の具体的構成を第3図に示してある。同図中、9a，9bはガスタンクであり、9aには窒素ガスが、又9bには水素ガスが封入してある。該両ガスタンクからの配管の途中には流量調整器10a，10bが設けてあり、両ガスの混合比率を調整できる。両調整器を出たガスは混合され流量調整器11を介して気密容器1へ向けて供給される。一方、窒素ガスのタンク9aからは流量調整器12を介してバブリング容器13内に窒素ガスが導入され、該容器内の液体合金14、例えばTiclが該ガスにより気化され、前記窒素と水素の混合ガスと混合されて気密容器1内のガスノズル7に導入される。尚、バブリングの仕方は上記に限定されるものではなく、加熱を併用したり、加熱を主体にするようなものでも良い。

15は前記被処理材料5とガスノズル7との間に配設された数個の熱電子陰極であり、例えばタングステンのコイルで形成されている。該熱電子陰極は電気絶縁物を介して容器外に取出され、昇圧トランス16を介して交流加熱電源17に接続されている。前記昇圧トランスの2次側中性点は

直流電源１８の負端子に接続され、気密容器及びガスノズルに対して負の電位に保持される。第４図はガスノズル７、熱電子陰極１５、被処理材料５のポテンシャルを示してあり、熱電子陰極は－１２０Ｖに、被処理材料５は－５２０Ｖに保持されている。

上記構成の装置の動作を次ぎに説明する。

気密容器１内のホルダー４上に被処理材料５を載置し、該気密容器内を真空ポンプ３により排気する。その後、第３図に示すガス導入源８の各流量調整器１０ａ，１０ｂ，１１，１２を調整して窒素ガス、水素ガス及び液体金属のガスの混合比を調整して気密容器１内に導入する。この様にして容器内を所望の圧力（10^{-1}～２０Ｔｏｒｒ）のガス雰囲気にする。この状態で直流高圧電源６により容器１と被処理材料５との間に２００Ｖ～数ＫＶの電圧を印加し、容器内に直流グロー放電（主グロー放電）を発生させる。同時に熱電子陰極１５に電源１７より加熱電流を供給して熱電子の発生が可能な程度の温度に加熱すると共に、直流電源１８より電子加速電圧を印加すると該熱電子陰極からの電子は該陰極よりプラス電位のガスノズル７に向けて飛翔する（熱陰極グロー放電と言う）。前記熱電子陰極１５と気密容器１との間の電圧は第４図に示すように例えば１２０Ｖ程度であり、被処理材料５と容器１との間の主グロー放電発生電圧、例えば５２０Ｖに比べ充分に低い電圧となしてある。

前記主グロー放電により発生したイオンは容器１と被処理材料５との間の電界により加速され、該材料に衝突し該材料を加熱する。そして、主グロー放電中に発生した金属イオンは被処理材料に引き付けられ、そのまま付着又は他のイオンと反応して金属化合物として付着する。この様な主グロー放電による薄膜付着のレートは前述の如く非常に低いわけであるが、本発明では主グロー放電とは別に熱電子陰極１５を使用した熱陰極グロー放電を発生しているので、前記主グロー放電によるイオンの発生に加えて熱電子陰極とガスノズルとの間で多量のイオンが発生し、該イオンが被処理材料に引付けられる。前記熱陰極グロー放電は被処理材料温度に直接関与しないので、あまり制限されることなく放電電力を高めることが可能である。そのため、主グロー放電のみの場合より気密容器内の金属ガスのイオン化が総体的に増大し、その分ガス圧を高めることができ、金属イオン数が増大し、薄膜付着レートを著しく増大することができる。

次に実験例について説明する。

〔１〕　従来の装置による実験例

ガス混合比	N_2 ＝30％，H_2 ＝60％，$TiCl_4$ ＝10％
処理温度	６００　℃
処理ガス圧	１　Ｔｏｒｒ
主グロー電圧	６００　Ｖ
付着レート	１２０　Å／ｍｉｎ

◎処理ガス圧をこれ以上高くすると未反応物が析出し、被膜を形成することができなくなる。

〔２〕　本発明装置による実験例

ガス混合比	N_2 ＝30％，H_2 ＝60％，$TiCl_4$ ＝10％
処理温度	６００　℃
処理ガス圧	４　Ｔｏｒｒ
主グロー電圧	５２０　Ｖ
熱電子陰極温度	２２００　℃
熱陰極グロー電圧	１２０　Ｖ
付着レート	３００　Å／ｍｉｎ

以上の両実験例から解るように、本発明によればガス圧を高めることが可能であり、その結果付着レートを従来の約３倍に増大することができ、金属化合物被膜の迅速な生成が可能となる。

尚、上記は本発明の一実施例であり実用に当っては種々な変更が可能である。例えば、熱陰極は第１図、第２図に示すような構造に限られず、有効な熱陰極グロー放電が可能であればどの様なものでも良く、第５図の様な輪状の陰極を複数個用いても良い。又、実験例に使用したガスや金属ガスの種類、各種の値等はこれに限定されるもので

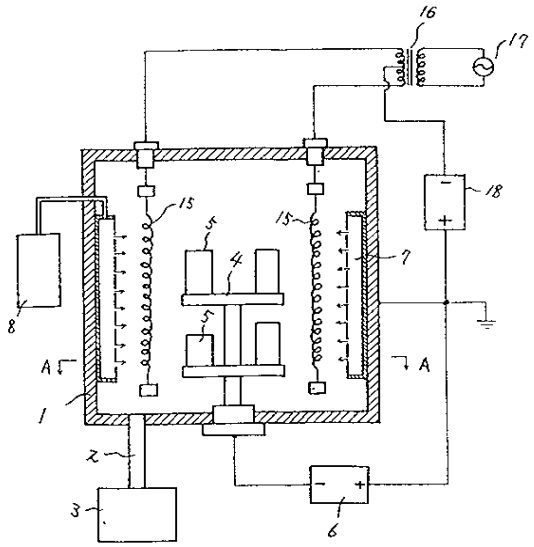
はない。

4．図面の簡単な説明

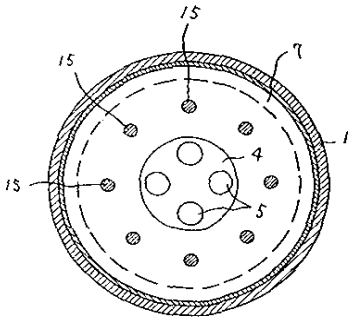
第1図は本発明の一実施例を示す構成略図、第2図は第1図装置のA－A線断面図、第3図は第1図装置の一部具体例を示す図、第4図は第1図装置の主要部の電位勾配を示す図、第5図は第1図装置の一部の他の例を示す図である。

1…気密容器
3…真空ポンプ
4…ホルダー
5…被処理材料
6…直流高圧電源
7…ガスノズル
8…ガス導入源
15…熱電子陰極
16…昇圧トランス
17…加熱電源
18…直流電源

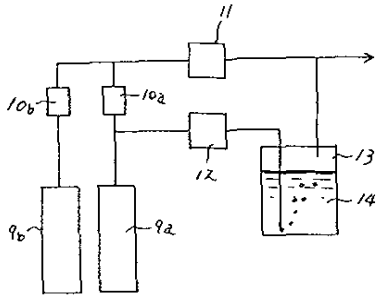
第1図



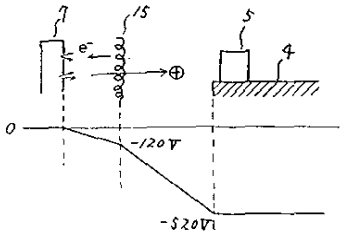
第2図



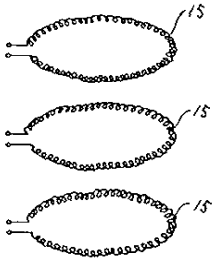
第3図



第4図



第5図



(54) PLASMA CVD PROCESSING APPARATUS
(11) 60-16419 (A) (43) 28.1.1985 (19) JP
(21) Appl. No. 58-124944 (22) 8.7.1983
(71) NIHON DENSHI KOGYO K.K. (72) TADASHI MATSUZAWA
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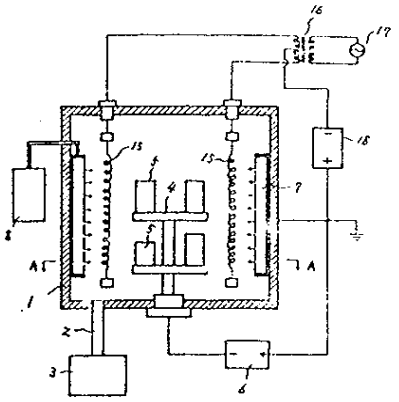
PURPOSE: To obtain a film in the sufficient thickness within a short period of time by putting a material to be processed into a hermetically sealed reservoir and supplying a film forming gas, generating DC plasma between the cathode made of a material to be processed and the anode made of reservoir, providing a hot electron cathode between the reservoir and material at the time of generating the desired film on the surface of material and by applying an intermediate voltage thereto.

CONSTITUTION: A multi-stage holder 4 is provided in a cylindrical sealed reservoir 1, many conductive material to be processed 5 are placed thereon, and a ring-shaped gas nozzle 7 is provided to the internal circumference of reservoir 1 while it is kept at the same potential as the reservoir 1. The reservoir 1 is vacuumed by an exhaust pipe 2 connected to a vacuum pump 3 and a raw gas for filming is sent thereto from a gas source 8. Thereafter, the negative terminal of external DC voltage source 6 is connected to the holder, namely to the material 5 and the positive terminal is connected to the reservoir 1 and is grounded. Moreover, a coiled hot electron cathode 15 is provided vertically between the nozzle 7 and material and an intermediate voltage sent from the AC heating power supply 17 through a boosting transformer 16 is applied to said cathode.



PTO 99-5345

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PLASMA CVD PROCESSING APPARATUS
[Purazuma CVD shori sochi]

Tadashi Matsuzawa

UNITED STATES PATENT AND TRADEMARK OFFICE
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INVENTOR	(72): MATSUZAWA, TADASHI
APPLICANT	(71): NIHON DENSHI KOGYO K.K.
TITLE	(54): PLASMA CVD PROCESSING APPARATUS
FOREIGN TITLE	[54A]: PURAZUMA CVD SHORI SOCHI

Specification

1. Title of the Invention

Plasma CVD processing apparatus

2. Claims

(1) A plasma CVD processing apparatus having a gas-tight vessel, a means for making the inside of that gas-tight vessel into a desired atmosphere, a processed material placed inside that gas-tight vessel, a DC high-voltage power supply that applies high-voltage electricity with that processed material as cathode and the gas-tight vessel as anode and generates a DC plasma, and a means for introducing a gas having constituents of a film to be formed on the surface of said processed material into said gas-tight vessel, wherein a hot electron cathode is provided between said gas-tight vessel and processed material, and there is furnished a DC power supply for applying to that hot electron cathode intermediate voltage between the gas-tight vessel and the processed material.

(2) A plasma CVD processing apparatus as defined in Claim 1, wherein a gas spraying nozzle is formed following the inner surface of said gas-tight vessel, said hot electron cathode is provided between that nozzle and the processed material, and a hot electron discharge is made toward that nozzle.

(3) A plasma CVD processing apparatus as defined in Claim 2, wherein said nozzle is ring-shaped, and it sprays mixed gas containing a desired gas and film constituents.

(4) A plasma CVD processing apparatus as defined in any of Claim 1 through Claim 3, wherein said hot electron cathode is placed as a plurality.

3. Detailed Explanation of the Invention

The present invention relates to a plasma CVD processing apparatus that ionizes a halogen compound or fluoride compound of a metal by direct current glow discharge and generates a film of metal or metal nitride, carbide, and the like on the surface of a processed material.

In recent times, so-called plasma CVD processing apparatuses (apparatuses for chemical gas-phase deposition in plasma), which perform deposition of films of metal compounds and the like by using irradiation of ions in a plasma, have attracted attention since the quality of the deposited films is very good compared with vacuum deposition, and they are already starting to enter into the stage of practical use.

In a plasma CVD apparatus using direct current glow discharge, the processed material is heated by kinetic energy having ions of the glow discharge, and a thin film of a desired compound is formed on the surface of the processed material by ionizing the introduced gas, being nitrogen gas, hydrogen gas, and a halogen compound or fluoride compound of metal, but in order to increase the ionization of the metal molecules, the average electron temperature must be raised as much as possible. This average electron temperature is represented by:

$$Te = q / k \; 0.3 \sqrt{} \; Mm / Me \; \lambda e \; E / P$$

Here, q is the electron charge, k is the Boltzmann constant, Mm and Me are respectively the mass of the gas molecules and the electrons, λe is

a free process of electrons at 0°C and 1 Torr, E is the electric field strength, and P is the pressure.

By the above formula, the average electron temperature Te is governed by the E / P parameter, but there is a limit to making E larger, and from the past, pressure P was made smaller in order to make Te larger.

However, even when doing thus, the ionization rate by direct current glow discharge is low and does not exceed as much as several %, therefore the adhesion rate of thin film is very low. In the case of plasma CVD, because the quantity of introduced gas is dependent on the ionization rate or plasma power, when the gas pressure is raised and excess gas is introduced in the attempt to increase the adhesion rate, unreacted substances are deposited, and it is difficult to form as a film. Accordingly, it is an important condition that the gas pressure be lowered, but when the gas pressure is low, it is inconvenient that the negative glow width becomes wider, and the vicinity of the corner parts of the processed material becomes poor.

The present invention aims to provide a plasma CVD processing apparatus that solves the abovementioned problems of the past, attempts acceleration of the adhesion of film in plasma CVD processing, and can form a uniform film layer of sufficient thickness in a short time.

The constitutive characteristics of the present invention are in a plasma CVD processing apparatus having a gas-tight vessel, a means for making the inside of that gas-tight vessel into a desired atmosphere, a processed material placed inside that gas-tight vessel, a DC high-voltage power supply that applies high-voltage electricity with that

processed material as cathode and the gas-tight vessel as anode and generates a DC plasma, and a means for introducing a gas having constituents of a film to be formed on the surface of said processed material into said gas-tight vessel, wherein a hot electron cathode is provided between said gas-tight vessel and processed material, and there is furnished a DC power supply for applying to that hot electron cathode intermediate voltage between the gas-tight vessel and the processed material.

The present invention is explained in detail below based on drawings.

Figure 1 is a component diagram of one working example of the present invention, and Figure 2 is a sectional view in the A-A line of Figure 1. 1 indicates a gas-tight vessel. That gas-tight vessel is connected to a vacuum pump 3 by way of an exhaust pipe 2, and the inside is capable of being drawn to a high vacuum. Said gas-tight vessel is cylindrically shaped as is clear from Figure 2, and an electrically conductive processed material holder 4 is placed in the center part thereof. This holder has a large number of processed materials 5 stacked on it. Said holder 4 is connected to gas-tight vessel 1 by way of an electrically insulating material, and the negative terminal of a DC high-voltage power supply 6 is connected to it. The positive terminal of that high-voltage power supply is connected to gas-tight vessel 1, and it is grounded. A ring-shaped gas nozzle 7 is provided in contact with the inner surface of said gas-tight vessel and at the same potential, and gas necessary for plasma CVD being introduced from a gas introduction source 8 outside the vessel is sprayed toward the center of

the vessel through a large number of fine holes. A specific configuration of said gas introduction source is shown in Figure 3. In the same drawing, 9a and 9b are gas tanks, and 9a is filled with nitrogen gas and 9b with hydrogen gas. Mid-course of piping from both of those gas tanks, there are provided flow regulators 10a and 10b, and the mixture ratio of both gases can be regulated. The gases coming out of both regulators are mixed and are supplied to gas-tight vessel 1 by way of flow regulator 11. Meanwhile, from nitrogen gas tank 9a, nitrogen gas is introduced into a bubbling vessel 13 by way of flow regulator 12, a liquid alloy 14 inside that vessel, such as $TiCl_4$, is gasified by that gas, it is mixed with said mixed gas of nitrogen and hydrogen, and it is introduced into gas nozzle 7 inside gas-tight vessel 1. The manner of the bubbling vessel is not limited to the abovementioned, and it may be one combining heating or one that mainly performs heating.

15 is a plurality of hot electron cathodes disposed between said processed material 5 and gas nozzle 7, and it is formed, for example, with a tungsten coil. That hot electron cathode is led out from the vessel by way of an electrically insulating material, and it is connected to an AC heating power supply 17 by way of a boosting transistor 16. The neutral point on the secondary side of said boosting transistor is connected to the negative terminal of a DC power supply 18, and it is kept to negative potential with respect to the gas-tight vessel and the gas nozzle. Figure 4 shows the potential of gas nozzle 7, hot electron cathode 15, and processed material 5, and the hot electron cathode is kept to -120 V and processed material 5 to -520 V.

The operation of the apparatus of the abovementioned configuration

is explained next.

Processed materials 5 are stacked on top of holder 4 inside gas-tight vessel 1, and the inside of that gas-tight vessel is exhausted by vacuum pump 3. After that, the mixture ratio of nitrogen gas, hydrogen gas, and liquid metal gas is regulated by adjusting each flow regulator 10a, 10b, 11, 12 of gas introduction source 8 shown in Figure 3, and they are introduced into gas-tight vessel 1. Doing thus, the inside of the vessel is made into a gas atmosphere of the desired pressure (10^{-1} - 20 Torr). In this state, 200 V - several KV of voltage is applied between vessel 1 and processed material 5 from DC high-voltage power supply 6, and a DC glow discharge (main glow discharge) is generated inside the vessel. At the same time, when heating current is supplied to hot electron cathode 15 from power supply 17 such that it is heated to a temperature to the extent that generation of hot electrons is possible, and electron accelerating voltage is applied from DC power supply 18, electrons from that hot electron cathode leap from that cathode toward gas nozzle 7 having plus potential (called hot cathode glow discharge). The voltage between said hot electron cathode 15 and gas-tight vessel 1 is about 120 V, for example, as shown in Figure 4, and it is a sufficiently low voltage compared with the voltage, such as 520 V, generated by the main glow discharge between processed material 5 and vessel 1.

The ions generated by said main glow discharge are accelerated by the electrical field between vessel 1 and processed material 5, and they collide with that material and heat that material. Also, the metal ions generated in the main glow discharge are attracted to the processed

material, and they adhere as they are or adhere as a metal compound reacting with other ions. The rate of thin film adhesion by such main glow discharge is very low as discussed before, but in the present invention, because a hot cathode glow discharge using hot electron cathode 15 is generated separately from the main glow discharge, a large volume of ions is generated between the hot electron cathode and the gas nozzle in addition to the generation of ions by said main glow discharge, and those ions are attracted to the processed material. Because the aforementioned hot cathode glow discharge does not directly contribute to the temperature of the processed material, it is possible to raise the discharge power without being constrained so much. Therefore, the ionization of the metal gas inside the gas-tight vessel is increased on the whole more so than just by the main glow discharge and the gas pressure can be raised by that much, and the number of metal ions is increased and the thin film adhesion rate can be markedly increased.

Next, working examples are explained.

[1] Working example with apparatus of the past

Gas mixture ratio	N_2 = 30%, H_2 = 60%, $TiCl_4$ = 10%
Processing temperature	600°C
Processing gas pressure	1 Torr
Main glow voltage	600 V
Adhesion rate	120 Å/min

* If processing gas pressure is made higher than this, unreacted substances are deposited, and a film can no longer be formed.

[2] Working example with apparatus of the present invention

Gas mixture ratio	N_2 = 30%, H_2 = 60%, $TiCl_4$ = 10%
Processing temperature	600°C
Processing gas pressure	4 Torr
Main glow voltage	520 V
Hot electron cathode temperature	2200°C
Hot cathode glow voltage	120 V
Adhesion rate	300 Å/min

As is clear from the above quantities, according to the present invention, it is possible to raise the gas pressure, and as a result, the adhesion rate can be increased to about 3 times that of the past, and fast formation of films of metal compounds becomes possible.

The abovementioned is one working example of the present invention, and various modifications are possible in practical use. For example, the hot cathode is not limited to the structure as shown in Figure 1 and Figure 2, it can be any kind of thing as long as an effective hot cathode glow discharge is possible, and a plurality of wheel-shaped cathodes as shown in Figure 5 may also be provided. Also, the types of gases and metal gases and the values of each type used in the working example are not limited to these.

4. Brief Explanation of the Figures

Figure 1 is a component diagram showing one working example of the present invention, Figure 2 is a sectional view in the A-A line of the apparatus in Figure 1, Figure 3 is a drawing showing a specific example of a part of the apparatus in Figure 1, Figure 4 is a drawing showing

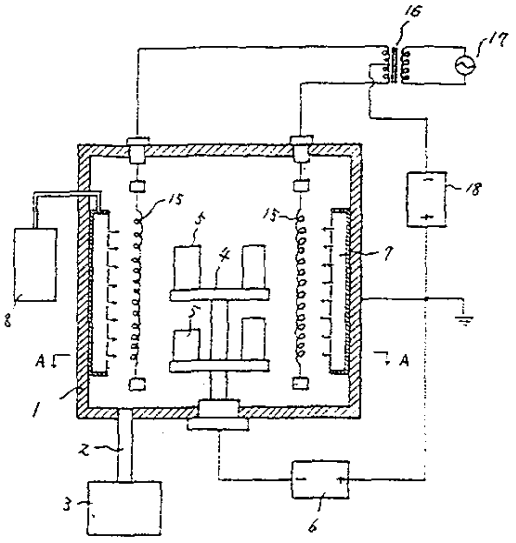

Figure 1

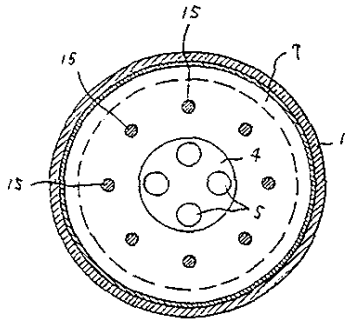

Figure 2

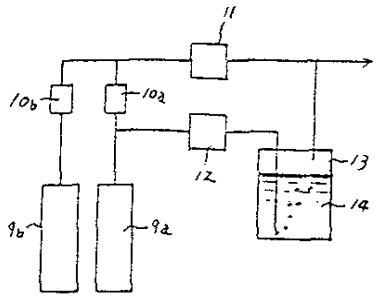

Figure 3

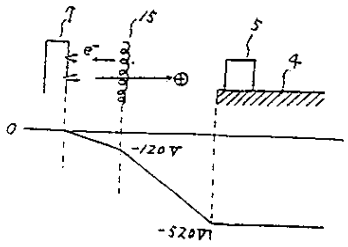

Figure 4

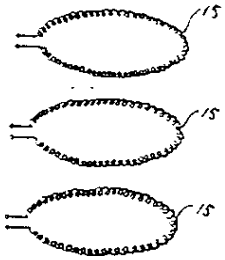

Figure 5